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### (54) PHOTOPOLYMERIZABLE COMPOSITION

PHOTOPOLYMERISIERBARE ZUSAMMENSETZUNG

COMPOSITION PHOTOPOLYMERISABLE

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(56) References cited:  
EP-A-0 339 841 EP-A-0 408 227  
JP-A-58 029 803 JP-A-60 076 735  
JP-A-60 076 740 JP-A-60 078 443  
JP-A-60 092 302 JP-A-60 096 604

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The file contains technical information submitted  
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specification

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**Description****Technical Field**

5 The present invention relates to a photopolymerizable composition having sensitivity to a visible ray or near infrared ray.

**Background Art**

10 Regarding photopolymerizable compositions having sensitivity to a visible ray, since drawing can be directly conducted using a laser beam as a light source, they are expected to be used as printing materials or photosensitive materials for hologram.

To these photopolymerizable compositions, dyes having absorption at visible ray or near infrared ray range are generally added as a sensitizer for imparting sensitivity to a visible ray.

15 Accordingly, these photopolymerizable compositions are colored depending on a dye contained.

These photopolymerizable composition can not be used in the field wherein clear transparency is required, for example hologram.

20 As a method for solving such a problem, for example, there is a method of using cyanine dyes as a sensitizer for photopolymerizable compositions, which is disclosed in Japanese (JP) Patent Kokai Nos. 58-29803 and 61-213838. Since cyanine dyes are liable to cause decoloring or fading by light irradiation, a clear transparent hologram can be obtained by using photopolymerizable compositions disclosed in the above references.

However, these photopolymerizable compositions have a disadvantage that storage stability is inferior.

Further photosensitive compositions are disclosed in EP-A-0 339 841 and EP-A-0 408 227.

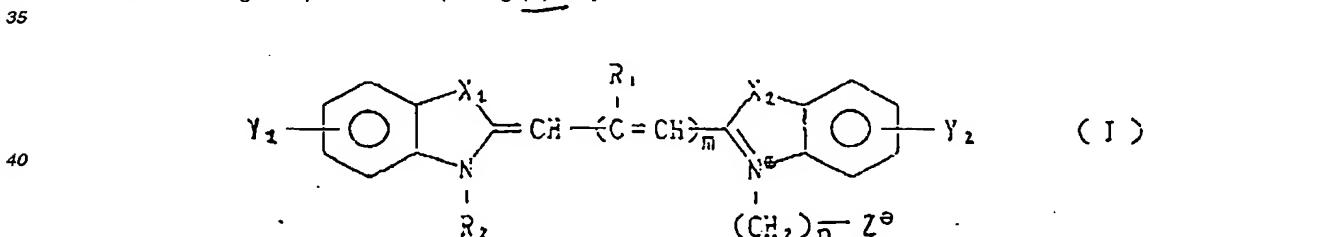
25 The present invention has been completed in order to solve the above problems and the object thereof is to provide a photopolymerizable composition having excellent storage stability and excellent sensitivity to a visible ray (particularly, a visible ray having a wavelength of not more than 550 nm), which is capable of decoloring by light irradiation.

**Disclosure of the Invention**

30 Subject matter of the present invention is a photopolymerizable composition according to Claim 1.

A preferred embodiment thereof is subject matter of Claim 2.

The present invention provides a photopolymerizable composition comprising an addition polymerizable compound having an ethylenically unsaturated double bond and a photopolymerization initiating composition, said photopolymerizable initiating composition comprising (a) a dye of the formula:



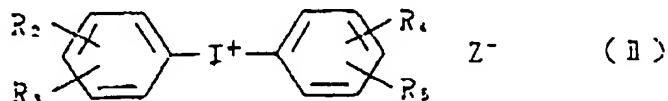
40 45 [wherein R<sub>1</sub> is H, an alkyl group having 1 to 3 carbon atoms, a phenyl group or a halogen atom; R<sub>2</sub> is a methyl group, an ethyl group or (CH<sub>2</sub>)<sub>p</sub>-Q (wherein Q is a carboxyl group, a sulfonyl group or salt thereof and p is an integer of 1 to 4); X<sub>1</sub> and X<sub>2</sub> are independently -O-, -S-, -CH=CH- or >N-R<sub>2</sub>; Y<sub>1</sub> and Y<sub>2</sub> are independently H, an alkyl group having 1 to 3 carbon atoms, an alkoxy group having 1 to 3 carbon atoms, a phenyl group or a halogen atom; Z is -COO or -SO<sub>3</sub>; m is 0 or 1; and n is an integer of 1 to 4] and (b) diaryliodonium salt as a polymerization initiator, whereby, the above object can be accomplished.

50 55 The dye (a) as a sensitizer to be formulated in the photopolymerizable composition of the present invention is the compound of the above formula (I), and examples thereof include 3,3'-dicarboxymethyl-2,2'-thiacyanine inner salt, 3,3'-dicarboxyethyl-5,5',9-trimethyl-2,2'-thiacarbocyanine inner salt, 3,3'-dicarboxymethyl-5,5'-dimethoxy-2,2'-thiacyanine inner salt, 3,3'-dicarboxymethyl-5,5'-dichloro-2,2'-thiacyanine inner salt, 3-ethyl-3'-carboxymethyl-2,2'-thiacyanine inner salt, 1-ethyl-3'-carboxymethyl-2,2'-quinothiacyanine inner salt, 1,3'-carboxymethyl-2,2'-quinothiacyanine inner salt, 1-ethyl-4-methoxy-3'-carboxymethyl-5'-chloro-2,2'-quinothiacyanine inner salt, 1-ethyl-4-methoxy-3'-(4-sulfonylbutyl)-2,2'-quinothiacyanine inner salt, 1-ethyl-(4-sulfonylbutyl)-5,5'-dichloro-2,2'-quinothiacyanine inner salt, anhydro-5,5'-diphenyl-9-ethyl-3,3'-disulfonylpropylloxacarbocyanine hydroxide triethylamine salt, anhydro-5,5'-dichloro-9-ethyl-3,3'-di-

sulfopropylloxacarbocyanine sodium salt, 1-carboxymethyl-1'-carboxyethyl-2,2'-quinothiacyanine inner salt, and 1,1-diethyl-3,3'-dicarboxymethyl-5,6,5',6'-tetrachloro-2,2'-benzimidazolocarbocyanine inner salt.

The diaryliodonium salt (b) as a polymerization initiator to be formulated in the photopolymerizable composition of the present invention is the compound of the formula:

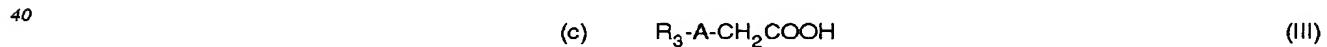
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[wherein R<sub>2</sub> to R<sub>5</sub> are independently hydrogen atom, halogen atom (e.g. chlorine, and fluorine), lower alkyl group (e.g. methyl, ethyl, propyl, and t-butyl), lower alkoxy group (e.g. methoxy, ethoxy, and propoxy) or nitro group; Z<sup>-</sup> is halogen ion (e.g. Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>), hydroxyl ion, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> or SbF<sub>6</sub><sup>-</sup>]. Examples of the compound represented by the formula (II) include chlorides, bromides, perchlorates, trifluoromethylsulfonates, tetrafluoroborates, hexafluorophosphates, hexafluoroarsenates, and hexafluoroantimonates, of iodoniums such as diphenyliodonium, bis(p-chlorophenyl)iodonium, ditolylodonium, bis(p-t-butylphenyl)iodonium, and bis(m-nitrophenyl)iodonium.

20 The photopolymerizable composition of the present invention can be essentially obtained by formulating a dye (a) as a sensitizer and a diaryliodonium salt (b) into an addition polymerizable compound (d) having an ethylenically unsaturated double bond. Regarding the addition polymerizable compound having an ethylenically unsaturated double bond, the addition polymerization is initiated by the effect of a photopolymerization initiation composition upon light irradiation and, as a result, the part irradiated is cured and is substantially insolubilized. Examples of the compound include unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid, and maleic acid esters of 25 polyhydroxy compounds (e.g. ethylene glycol, tetraethylene glycol, neopentylglycol, propylene glycol, 1,2-butanediol, trimethylolpropane, and pentaerythritol, tripentaerythritol) with the above unsaturated carboxylic acids; addition reaction products of epoxide compounds (e.g. trimethylolpropane polyglycidyl ether, pentaerythritol polyglycidyl ether, and propylene glycol diglycidyl ether) with the above unsaturated carboxylic acids; polyurethane acrylates and polyurethane 30 methacrylates synthesized from polyfunctional isocyanate compounds (e.g. hexamethylene diisocyanate, 2,4-toluene diisocyanate, isophorone diisocyanate, 4,4'-methylenebis(phenylisocyanate)), acrylic esters or methacrylic esters having a hydroxyl group (e.g. 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, and 2-hydroxypropyl methacrylate) and the above polyhydroxy compounds; acrylamides and methacrylamides such as acrylamide, ethylene-bis-acrylamide, ethylene-bis-methacrylamide, hexamethylene-bis-acrylamide, and hexamethylene-bis-methacrylamide. Preferably, acrylic esters or methacrylic esters are used.

35 The photopolymerizable composition having sufficient sensitivity is normally obtained from a composition comprising a dye (a), a diaryliodonium salt (b) and an addition polymerizable compound (d) having an ethylenically unsaturated double bond. When higher sensitivity is required, it is preferred to further formulate an auxiliary sensitizer (c) of the formula (III):



[wherein R<sub>3</sub> is a phenyl group or a substituted phenyl group and A is -O-, -S-, a secondary nitrogen atom or a tertiary nitrogen atom].

45 Examples of this compound include phenoxyacetic acid, O-chlorophenoxyacetic acid, N-phenylglycine, N-(P-methoxyphenyl)glycine, N-(P-chlorophenyl)glycine, N-hydroxyethyl-N-phenylglycine, and N-(2-hydroxy-3-methacryloxy-propyl)-N-phenylglycine.

50 The amount of the component (a) is 0.001 to 0.1 parts by weight, preferably 0.004 to 0.03 parts by weight and the amount of the components (b) and (c) is 0.01 to 0.2 parts by weight, preferably 0.03 to 0.1 parts by weight, respectively, based on 1 part of the component (d). The amount of the component (a) varies depending upon a thickness of the photopolymerizable composition to be applied. When the amount of the components (a), (b) and (c) is less than the above range, sensitivity is deteriorated and it takes a long time to insolubilize (cure) the composition. When the amount is more than the above range, storage stability is deteriorated, or strength and solvent scubility resistance of the film formed are deteriorated.

55 The photopolymerizable composition of the present invention may contain, if necessary, polymer binders, thermopolymerization inhibitors, plasticizers, and colorants. The polymer binders are used for improving various properties such as compatibility, film-forming property, and adhesion property, and suitable kinds of them may be used according

to the objects.

The composition of the present invention may be prepared by a normal method. For example, it can be prepared by formulating the above essential components as they are, or optionally formulating the components together with a solvent [e.g. ketone solvents such as methyl ethyl ketone, acetone, and cyclohexanone; ester solvents such as ethyl acetate, butyl acetate, and ethylene glycol diacetate; aromatic solvents such as toluene, and xylene; cellosolve solvents such as methyl cellosolve, ethyl cellosolve, and butyl cellosolve; alcohol solvents such as methanol, ethanol, and propanol; ether solvents such as tetrahydrofuran, and dioxane; halogen solvents such as dichloromethane, and chloroform] and mixing them in a dark place, for example, with a high speed mixer.

The photosensitive layer can be formed by applying the photosensitive composition of the present invention on a substrate, for example, with a bar coater, applicator or spinner and drying according to a normal method. Further, a known technique for protecting the surface and preventing bad influence such as deterioration of sensitivity due to oxygen may be applied to the photosensitive layer formed. For example, a peelable transparent cover sheet or a coating layer made of wax-like substance having water-soluble or alkaline water-soluble polymer can be provided on the photosensitive layer.

As the light source used for light irradiation, there can be used conventional light sources generating a visible ray or ultraviolet ray, for example, lasers such as argon laser, helium-cadmium laser, helium-neon laser, krypton laser and semiconductor laser, ultrahigh pressure mercury lamp, high pressure mercury lamp, moderated mercury lamp, low pressure mercury lamp, metal halide lamp, and tungsten lamp. Further, in the case of removing the photosensitive layer of the non-exposed part after light irradiation, a suitable developing solution capable of dissolving the photosensitive layer of the non-exposed part may be used.

In the photopolymerizable composition of the present invention, the color of the dye (a) can be removed by light irradiation. Accordingly, the composition can be suitably used for producing hologram wherein transparency is required, and diffraction grating. For example, in the case of producing the hologram, the photosensitive resin plate made by using a transparent substrate such as glass plate and the photopolymerizable composition of the present invention is firstly subjected to a predetermined operation to form an interference fringe of holography. The hologram thus obtained has been colored with the dye (a) as a sensitizer. However, the color of the hologram is removed by additional light irradiation, whereby, a hologram having excellent transparency can be obtained.

In addition to the above applications, the photopolymerizable composition of the present invention can be suitably used for various applications such as normal printing plate, photopolymerizable paint, and photoresist for producing print circuit board.

### Example

The following Examples further illustrate the present invention in detail.

#### Examples 1 to 11

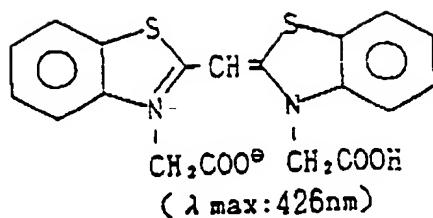
In these Examples, sensitivity and storage stability of the photosensitive resin plate made by using the photopolymerizable composition of the present invention will be explained. In the Examples, all "parts" are by weight unless otherwise stated.

#### Preparation of photopolymerizable composition

100 Parts of an acrylic polymer having a weight-average molecular weight of 48,000 and an acid value of 75 (trade name of Carboset XL-44, manufactured by BF Goodrich Co.) was dissolved in 700 parts of methyl ethylketone. To the mixture, 100 parts of pentaerythritol triacrylate was dissolved to obtain the first solution.

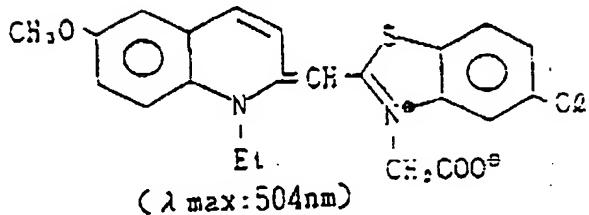
Then, dyes of the following formulas and maximum absorption wavelength  $\lambda_{max}$  A-1 to A-4, polymerization initiators of the following formulas B-1, B-2 and B-3, and auxiliary sensitizers of the following C-1 and C-2 are respectively dissolved in a mixed solution of 300 parts of methylcellosolve and 300 parts of ethyl alcohol in a ratio shown in Table 1 to form the second solution. Total amount of each solution was added to the first solution and sufficiently stirred to obtain a solution of the photopolymerizable composition (photosensitive solution). Further, when insolubles are produced in the composition, they were filtered off.

5 A-1:



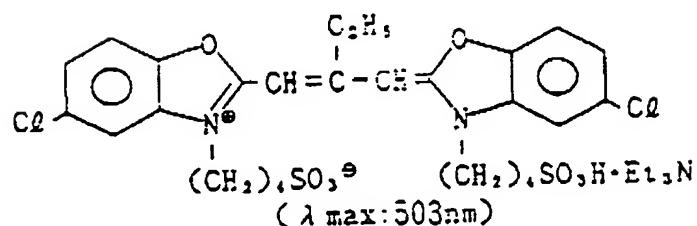
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15 A-2:



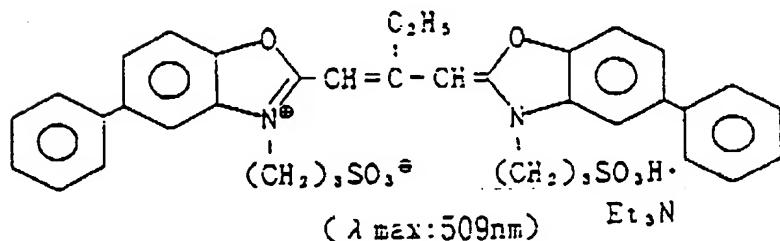
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25 A-3:



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35 A-4:



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50 B-1: Diphenyliodonium chloride

B-2: Diphenyliodonium tetrafluoroborate

55 B-3: 4,4'-Ditertiarybutyldiphenyliodonium hexafluoroantimonate

C-1: N-phenylglycine

## C-2: N-Hydroxyethyl-N-phenylglycine

Preparation of photosensitive resin plate

5 The above photosensitive solution was applied on an aluminum substrate using a bar coater so that the amount of coating becomes 2 g/m<sup>2</sup> on drying, and dried in a drying oven at 60°C for 3 minutes. A photosensitive layer having a thickness of 2.0 μm was obtained. Further, an aqueous 5 % polyvinyl alcohol (saponification degree of 88 %, polymerization degree of 500) was applied on the photosensitive layer using a bar coater so that the thickness becomes 10 2 μm on drying to form an overcoat layer, whereby, a photosensitive resin plate was obtained.

Measurement of sensitivity and storage stability

15 The each photosensitive resin plate was piled with Step Tablet No. 2 (21 steps) manufactured by Kodak Co. and irradiated for 30 seconds with the light (light intensity of 4.0 mW/cm<sup>2</sup>) having a wavelength of 430 nm which was taken out from a xenon lamp (150 W) manufactured by Ushio Denki K.K. through TOSHIBA KL-43 filter, or with the light (light intensity of 4.0 mW/cm<sup>2</sup>) having a wavelength of 490 nm which was taken out through TOSHIBA KL-49 filter. Thereafter, 20 the non-cured part of the irradiated photosensitive resin plate was eluted in an aqueous 1 % sodium carbonate and sensitivity was evaluated by the number of cured steps. Further, in order to determine storage stability of the photosensitive resin plate, sensitivity changes of the photosensitive resin plate after storage in a dark place at room temperature of 40°C for 50 days was measured. The results of sensitivity and storage stability are shown in Table 1.

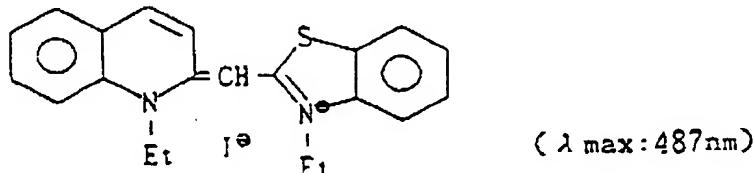
25 As is apparent from the results shown in Table 1, a photosensitive resin plate made by using the photopolymerizable composition of the present invention is superior in sensitivity to a visible ray having a wavelength at 400 to 500 nm and in storage stability.

Comparative Examples 1 to 4

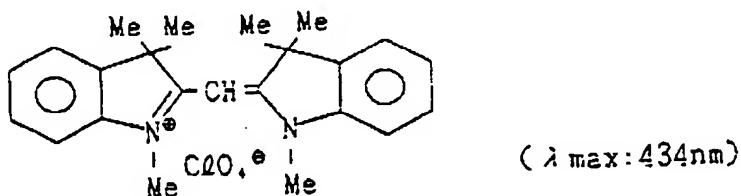
30 In these Comparative Examples, sensitivity and storage stability of the photosensitive resin plate made by using the conventional photopolymerizable composition will be explained.

35 According to the same manner as that described in Examples 1 to 11 except for using cyanine dyes of the formulas A'-1, A'-2 and A'-3 and having  $\lambda_{\text{max}}$  at the same wavelength range as that of the dye used in the present invention, a photopolymerizable composition and photosensitive resin plate were made, and sensitivity and storage stability were determined. The results are shown in Table 1.

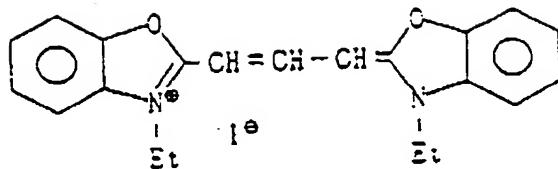
40 A'-1:



45 A'-2:



A' - 3:



(λ max: 484nm)

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10 As is apparent from Table 1, a photosensitive resin plate made by using the conventional photopolymerizable composition is inferior in sensitivity to a visible ray having a wavelength at 500 nm.

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Table 1

Photopolymerization initiating  
composition (parts by weight)<sup>1)</sup>

Sensitivity 2) (Number  
of cured steps)

Component (A)	Component (B)	Component (C)	Sensitivity 2) (Number of cured steps)	Storage stability (after storage at 40°C for 50 days)
Ex.1 A-1, 3 parts	B-1, 6 parts	-	10 <sup>3</sup> )	No change
Ex.2 A-1, 3 parts	B-2, 6 parts	-	10 <sup>3</sup> )	No change
Ex.3 A-2, 3 parts	B-1, 3 parts	-	11	No change
Ex.4 A-2, 3 parts	B-1, 6 parts	-	13	No change
Ex.5 A-2, 3 parts	B-3, 6 parts	-	9	No change
Ex.6 A-3, 3 parts	B-2, 6 parts	-	10	No change
Ex.7 A-4, 3 parts	B-1, 6 parts	-	9	No change

1): Ratio based on 100 parts by weight of pentaerythritol triacrylate [component (d)]

2): The larger the number, the higher sensitivity is.

3): Wavelength of irradiated light is 430 nm (that of others is 490 nm).

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Table 1 (continued)

Component (A)	Component (B)	Component (C)	Photopolymerization initiating composition (parts by weight)	Sensitivity 2) (Number of cured steps)		Storage stability (after storage at 40°C for 50 days)
				Ex.8	Ex.9	Ex.10
Comp. Ex.1	A'-1, 3 parts	B-1, 6 parts	C-1, 6 parts	12 <sup>3)</sup>	No change	No change
Comp. Ex.2	A'-1, 3 parts	B-1, 6 parts	C-1, 6 parts	15	No change	No change
Comp. Ex.3	A'-2, 3 parts	B-2, 6 parts	C-2, 3 parts	11	No change	No change
Comp. Ex.4	A'-3, 3 parts	B-1, 6 parts	C-2, 6 parts	11	No change	No change
Comp. Ex.5	A'-1, 3 parts	B-1, 6 parts	-	0	Not measured because no sensitivity is observed	Not measured because no sensitivity is observed
Comp. Ex.6	A'-1, 3 parts	B-1, 6 parts	C-1, 6 parts	0	Not measured because no sensitivity is observed	Not measured because no sensitivity is observed
Comp. Ex.7	A'-2, 3 parts	B-1, 6 parts	-	0 <sup>3)</sup>	Not measured because no sensitivity is observed	Not measured because no sensitivity is observed
Comp. Ex.8	A'-3, 3 parts	B-1, 6 parts	-	0	Not measured because no sensitivity is observed	Not measured because no sensitivity is observed

Example 12

In this Example, the fact that the hologram made by using the photopolymerizable composition of the present invention is easily decolored by light irradiation will be explained.

According to the same manner as that described in Examples 1 to 11 except for using the following formulation shown in Table 2, a photopolymerizable composition was prepared.

Table 2

10	Acrylic resin (BR-77, manufactured by Mitsubishi Rayon Co. Ltd.)	10 g
	Pentaerythritol triacrylate	8 g
15	Dye A-2	0.05 g
	Diphenyliodonium tetrafluoroborate	0.5 g
	Methyl ethyl ketone	30 g
	2-Methoxyethanol	20 g

Then, the photopolymerizable composition was applied on a glass plate as a substrate and dried to form a photosensitive layer. In that case, application of the photopolymerizable composition was conducted using an applicator so that a thickness of the resulting photosensitive layer becomes 5  $\mu\text{m}$  and drying was conducted at a temperature of 20 80°C for 5 minutes. An aqueous 10 % polyvinyl alcohol (GL-05, manufactured by Nihon Gosei Kagaku Co. Ltd.) was applied on the photosensitive layer and dried to form a polyvinyl alcohol layer having a thickness of 5  $\mu\text{m}$ , whereby, a photosensitive resin plate for hologram recording was obtained.

Thereafter, a light having a wavelength of 514.5 nm and an energy of 50  $\text{mJ/cm}^2$  was irradiated on the photosensitive resin plate using a two light flux interference optical device for producing hologram and an argon laser to form a pattern of an interference wave of holography. The photosensitive resin plate on which the pattern of the interference wave has been formed was subjected to a developing operation (dipping in an ethanol for 30 seconds and additional dipping in heptane for 30 seconds) to obtain a Lippmann type hologram.

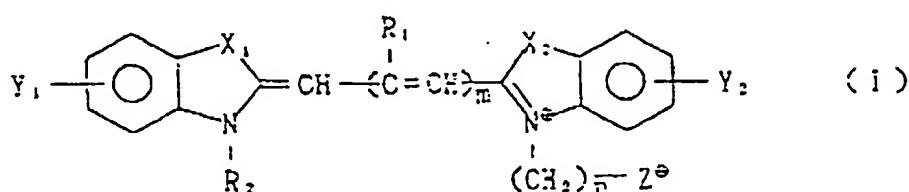
The resulting hologram was colored orange according to a dye A-2 used as a sensitizer of the photopolymerizable composition. However, the hologram was irradiated from the distance of 50 cm for 10 minutes using a 3 kW ultrahigh pressure mercury lamp and, as a result, hologram was decolored and it became transparent.

Effect of the Invention

According to the present invention, there is provided a photopolymerizable composition having excellent storage stability and excellent sensitivity to a visible ray (particularly, a visible ray having a wavelength of not more than 550 nm), which can provide a photosensitive resin plate capable of decoloring by light irradiation.

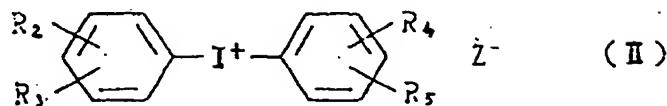
Claims

1. A photopolymerizable composition comprising an addition polymerizable compound having an ethylenically unsaturated double bond and a photopolymerization initiating composition, said photopolymerizable initiating composition comprising (a) a dye of the formula:



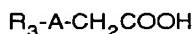
55 [wherein R<sub>1</sub> is H, an alkyl group having 1 to 3 carbon atoms, a phenyl group or a halogen atom; R<sub>2</sub> is a methyl group, an ethyl group or (CH<sub>2</sub>)<sub>p</sub>-Q (wherein Q is a carboxyl group, a sulfonyl group or salt thereof and p is an integer of 1 to 4); X<sub>1</sub> and X<sub>2</sub> are independently -O-, -S-, -CH=CH- or >N-R<sub>2</sub>; Y<sub>1</sub> and Y<sub>2</sub> are independently H, an alkyl group having 1 to 3 carbon atoms, an alkoxy group having 1 to 3 carbon atoms, a phenyl group or a halogen atom; Z is -COO or -SO<sub>3</sub>; n is 0 or 1; and n is an integer of 1 to 4] and (b) diaryliodonium salt with the following

formula as a polymerisation initiator



10 wherein R<sub>2</sub> to R<sub>5</sub> independently represent a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>4</sub>-alkyl atom, a C<sub>1</sub>-C<sub>3</sub> alkoxy group or a nitro group and Z<sup>-</sup> is a halogen ion, a hydroxyl ion, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> or SbF<sub>6</sub><sup>-</sup>, and wherein the amount of component (a) is 0.001 to 0.1 parts by weight, and the amount of component (b) is 0.01 to 0.2 parts by weight, based on 1 part of the addition polymerizable compound.

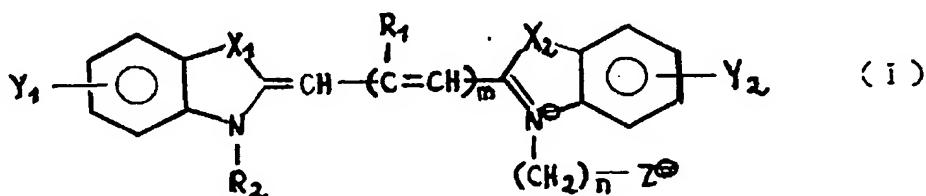
15 2. The photopolymerizable composition according to Claim 1, wherein the photopolymerization initiating composition further contains (c) an auxiliary sensitizer of the formula:



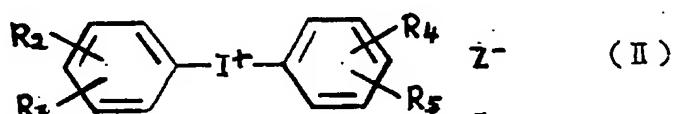
20 wherein R<sub>3</sub> is a phenyl group or a substituted phenyl group; and A is -O-, -S- a secondary nitrogen atom or a tertiary nitrogen atom.

25 **Patentansprüche**

1. Photopolymerisierbare Zusammensetzung, die eine durch Additionspolymerisation polymerisierbare Verbindung, welche eine ethylenisch ungesättigte Doppelbindung hat, und eine eine Photopolymerisation initiiierende Zusammensetzung enthält, wobei die eine Photopolymerisation initiiierende Zusammensetzung (a) einen Farbstoff der Formel:



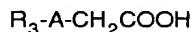
40 [in der R<sub>1</sub> H, eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen, eine Phenylgruppe oder ein Halogenatom ist; R<sub>2</sub> eine Methylgruppe, eine Ethylgruppe oder (CH<sub>2</sub>)<sub>p</sub>-Q (worin Q eine Carboxylgruppe, eine Sulfonylgruppe oder ein Salz derselben ist, und p eine ganze Zahl von 1 bis 4 ist) ist; X<sub>1</sub> und X<sub>2</sub> unabhängig voneinander -O-, -S-, -CH=CH- oder >N-R<sub>2</sub> sind; Y<sub>1</sub> und Y<sub>2</sub> unabhängig voneinander H, eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen, eine Alkoxygruppe mit 1 bis 3 Kohlenstoffatomen, eine Phenylgruppe oder ein Halogenatom sind; Z -COO oder -SO<sub>3</sub> ist; m 0 oder 1 ist; und n eine ganze Zahl von 1 bis 4 ist], und (b) Diaryliodoniumsalz mit der folgenden Formel



55 in der R<sub>2</sub> bis R<sub>5</sub> unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine C<sub>1</sub>-C<sub>4</sub>-Alkylgruppe, eine C<sub>1</sub>-C<sub>3</sub>-Alkoxygruppe oder eine Nitrogruppe darstellen; und Z ein Halogenion, ein Hydroxylion, HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> oder SbF<sub>6</sub><sup>-</sup> ist, als Polymerisationsinitiator enthält, wobei die Menge d r Komponente

(a) 0,001 bis 0,1 Gew.-Teile und die Menge der Komponente (b) 0,01 bis 0,2 Gew.-Teile, bezogen auf 1 Teil der durch Additionspolymerisation polymerisierbaren Verbindung, ist.

2. Photopolymerisierbare Zusammensetzung nach Anspruch 1, in der die eine Photopolymerisation initierende Zusammensetzung außerdem (c) einen Hilfsensibilisator der Formel

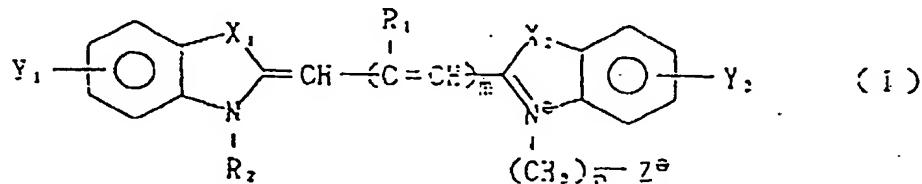


10 in der  $R_3$  eine Phenylgruppe oder eine substituierte Phenylgruppe ist, und A -O-, -S-, ein sekundäres Stickstoffatom oder ein tertiäres Stickstoffatom ist, enthält.

#### Revendications

15 1. Composition photopolymérisable comprenant un composé d'addition polymérisable ayant une double liaison éthyéniquement insaturée et une composition d'initiateur de photopolymérisation, ladite composition d'initiateur de photopolymérisation comprenant :

20 (a) un colorant de formule :



30 dans laquelle  $R_1$  est H, un groupe alkyle ayant de 1 à 3 atomes de carbone, un groupe phényle ou un atome d'halogène ;  $R_2$  est un groupe méthyle, un groupe éthyle ou  $(CH_2)_p-Q$  ( $Q$  étant un groupe carboxyle, un groupe sulfonyle ou un sel correspondant et  $p$  est un nombre entier de 1 à 4) ;

35  $X_1$  et  $X_2$  sont indépendamment -O-, -S-, -CH=CH- ou  $>N-R_2$  ;

40  $Y_1$  et  $Y_2$  sont indépendamment H, un groupe alkyle ayant de 1 à 3 atomes de carbone, un groupe alkoxy ayant de 1 à 3 atomes de carbone, un groupe phényle ou un atome d'halogène ;

45  $Z$  est -COO ou  $-SO_3$  ;  $m$  est 0 ou 1 ; et  $n$  est un nombre entier de 1 à 4 et

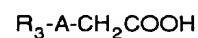
50 (b) un sel de diaryliodonium en tant qu'initiateur de polymérisation ayant la formule suivante :



55 dans laquelle  $R_2$  à  $R_5$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe alkyle en  $C_1-C_4$  un groupe alkoxy en  $C_1-C_3$  ou un groupe nitro et  $Z$  est un ion halogène, un ion hydroxyle,  $HSO_4^-$ ,  $ClO_4^-$ ,  $CF_3SO_3^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$  ou  $SbF_6^-$ , et dans laquelle la quantité du composant (a) est de 0,001 à 0,1 partie en poids et la quantité du composant (b) est de 0,01 à 0,2 partie en poids par rapport à une partie du composé d'addition polymérisable.

55 2. Composition photopolymérisable selon la revendication 1, dans laquelle la composition d'initiateur de polymérisation contient en outre (c) un sensibilisateur auxiliaire de formule :

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5 dans laquelle  $R_3$  est un groupe phényle ou un groupe phényle substitué ;  
A est -O-, -S-, un atome d'azote secondaire ou un atome d'azote tertiaire.

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